

## PATENT ABSTRACTS OF JAPAN

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**(54) LIQUID CHEMICAL FOR FORMING SILVER COATING FILM AND FORMATION OF SILVER COATING FILM****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To efficiently form a silver coating film with the silver deposition rate enhanced as compared with the conventional technique and to form a fine and dense silver coating film.

**SOLUTION:** The liq. chemical for forming a silver coating film consists of a soln. contg. ammoniacal silver nitrate and a reducing soln. contg. a reducing agent and a strongly alkaline component, and the materials are allowed to react with each other to form a silver coating film on a substrate. One or more kinds of alkali halides and  $\geq 1$  kind of water-soluble protein or the compound of the alkali halide and protein is incorporated into the reducing soln., and a silver coating film is formed from the chemical.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The drug solution for silver coat formation characterized by making said reducing solution contain more than a kind of alkali halides in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.

[Claim 2] The amount of a silver nitrate 0.1mol. It receives and the amount more than a kind of alkali halides Drug solution for silver coat formation according to claim 1 characterized by, preparing a silver solution and each reducing solution if possible with the quantitative ratio range which is 1-30mg, and making it contact both liquid on a substrate.

[Claim 3] The drug solution for silver coat formation characterized by making said reducing solution contain more than a kind of water-soluble protein in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.

[Claim 4] The amount of a silver nitrate 0.1mol. Drug solution for silver coat formation according to claim 3 characterized by receiving, preparing a silver solution and each reducing solution if possible with the quantitative ratio range more than whose a kind of water-soluble protein is 70-1200mg, and making it contact both liquid on a substrate.

[Claim 5] The drug solution for silver coat formation characterized by making more than a kind of alkali halides, and more than a kind of water-soluble protein coexist in said reducing solution in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.

[Claim 6] The amount of a silver nitrate 0.1mol. It receives and the amount more than a kind of alkali halides Drug solution for silver coat formation according to claim 5 characterized by 1-30mg and more than a kind of water-soluble protein, preparing a silver solution and each reducing solution if possible with the quantitative ratio range which is 70-1200mg, and making it contact both liquid on a substrate.

[Claim 7] The silver coat forming method characterized by to consist of a process which it contacts [ process ] and makes the process which some silver solutions which contain a silver nitrate for the hydrochloric-acid acid-salt-ized first tin solution on the occasion of formation of contact, the process which carries out conditioning, and a silver coat precede [ process ], and contacts it on a substrate on the pure substrate transported continuously, the silver solution which subsequently contain a silver nitrate, and the reducing solution containing a reducing agent and a strong-base component react simultaneously on a substrate.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention deposits a detailed silver granule child on substrates, such as glass, — making — a silver coat — forming — further — a copper coat and an anticorrosion resin coat — covering — a mirror — manufacturing — hitting — said silver coat — precise and homogeneity — plating — it is related with the approach of forming efficiently.

[0002]

[Description of the Prior Art] Contact, the drug solution for silver coat formation which consists of a reducing solution containing strong-base components, such as reducing agents, such as a silver solution containing an ammonia nature silver nitrate, sodium gluconate, a glucitol and grape sugar, a tartaric acid, and formaldehyde, and a sodium hydroxide, and a potassium hydroxide, is made to react on a substrate, and a deposit and carrying out coat formation are known in silver on the substrate.

[0003]

[Problem(s) to be Solved by the Invention] However, the rate of silver plating is low only by only contacting and making these components only react, and an efficient silver coat is not made, and a detail and a precise and uniform silver coat cannot be formed.

[0004] This invention has a high rate of silver plating, a detail and a precise and uniform silver coat are formed, and it aims at offering the silver coat forming method using the drug solution for silver coat formation and it by which a precise reflected image is therefore acquired.

[0005]

- [Means for Solving the Problem] This invention is 1. Drug solution for silver coat formation which made said reducing solution contain more than a kind of alkali halides in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.
- 2) The amount of a silver nitrate in the above 0.1mol. It receives and the amount more than a kind of alkali halides If possible, a silver solution and each reducing solution are prepared with the quantitative ratio range which is 1-30mg, and it was made to contact both liquid on a substrate.
- 3) The drug solution for silver coat formation which made said reducing solution contain more than a kind of water-soluble protein in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.
- 4) The amount of a silver nitrate in the above 0.1mol. It receives, if possible, a silver solution and each reducing solution are prepared with the quantitative ratio range more than whose a kind of water-soluble protein is 70-1200mg, and it was made to contact both liquid on a substrate.
- 5) The drug solution for silver coat formation which made more than a kind of alkali halides, and more than a kind of water-soluble protein coexist in said reducing solution in the drug solution for silver coat formation for consisting of a silver solution containing an ammonia

nature silver nitrate, and a reducing solution containing a reducing agent and a strong-base component, making these react, and forming a silver coat on a substrate.

6) The amount of a silver nitrate in the above 0.1mol. It receives and the amount more than a kind of alkali halides. If possible, 1-30mg and more than a kind of water-soluble protein prepare a silver solution and each reducing solution with the quantitative ratio range which is 70-1200mg, and it was made to contact both liquid on a substrate.

7) silver coat forming method. which consists of a process which it contacts [ process ] and makes the process which some silver solutions which contain a silver nitrate for the hydrochloric-acid acid-salt-ized first tin solution on the occasion of formation of contact, the process which carry out conditioning, and a silver coat precede [ process ], and contacts it on a substrate on the pure substrate transported continuously, the silver solution which subsequently contain a silver nitrate, and the reducing solution containing a reducing agent and a strong-base component react simultaneously on a substrate from -- it is constituted. [0006]

[Embodiment of the Invention] The silver solution in the drug solution for silver coat formation means the water solution containing a silver nitrate and ammonium hydroxide, and while is regularly used as liquid in silver coat formation.

[0007] A reducing solution means the water solution containing strong-base components, such as reducing agents, such as sodium gluconate, a glucitol, grape sugar, a tartaric acid, and formaldehyde, and a sodium hydroxide, and a potassium hydroxide, and it is regularly used as liquid of another side in silver coat formation.

[0008] A silver solution and a reducing solution are simultaneously injected and mixed on the substrate transported, for example, a transparence glass substrate, silver deposits by the reduction reaction, and a silver coat is formed on a substrate. In addition, in mirror manufacture, a copper coat is further formed by the same chemical-plating method, and a mirror is completed by giving a resin coat on it.

[0009] However, it sets on the conventional technique and is the aggregate (silver paint is called) of silver colloid in a solution in the middle of a plating reaction. Since it is generated, like point \*\*, the rate of silver plating is low and cannot form a detailed and precise silver coat efficiently. In this invention, on the occasion of formation of said silver coat, when carrying out film formation of the silver finely uniformly and efficiently, the effective drug solution for silver coat formation and the silver coat forming method are offered.

[0010] In this invention, the alkali halides a reducing solution is made to contain say meltable protein to the water with which water-soluble protein is represented by casein and gelatin in KI, NaI, KBr, NaBr, KCl, NaCl, etc. again. Suitably, alkali halides are in a water solution like water-soluble protein, it covers the silver colloid of unstable canal nature with mixing of an amount, and achieves the duty of the protective colloid which prevents silver paint, and uniform plating of the silver to a substrate is urged to it. In addition, if the alkali halide of an excess amount is mixed, since the evil in which silver paint is generated again and the debasement of silvering effectiveness or a mirror is caused will arise, caution is required.

[0011] The concentration of the silver nitrate in a silver solution makes 0.1 mol/L extent a criterion, and is 0.01 mol/L. Or 1 mol/L. What is necessary is just to choose suitably in the range. The alkali halides and the water-soluble protein in a reducing solution take into consideration and introduce the amount of said silver nitrate, the quantitative ratio of a silver solution and a reducing solution, etc., and are the amount of a silver nitrate. 0.1mol. It receives and alkali halides. It adjusts so that 1-30mg or water-soluble protein may serve as quantitative ratio range which is 70-1200mg. In said range, a good result is obtained in silvering effectiveness etc. In addition, also when making alkali halides and water-soluble protein coexist, it considers as above-mentioned within the limits.

[0012] Usually, for a silver solution and a reducing solution, equivalent [ every ], although it adopts and is made to contact and react on a substrate, it does not limit to this, and a silver solution:reducing solution is 1:1/2 mostly. \*\* [ there is nothing ] You may be 1/2:1.

[0013] The reaction time of a silver solution and a reducing solution be set even before or after 20 seconds of the first stage, when it be additive-free, inclinations differ by the case

where additives, such as alkali halides and water-soluble protein, be include in a reducing solution, and the case where these additives cannot be find, quickly, it react and carry out film formation, subsequent reactions hardly progress, but if you be going to make it react more for a long time, a film front face will present the condition of \*\* by a coarse silver granule child's sediment. When an additive is included, although based also on the class of additive, and an amount, a reaction progresses 40 seconds of the first stage, or till around that generally, film formation is carried out, and though it or subsequent ones is loose, a reaction advances. In addition, it is in the inclination for a film front face to present the condition of \*\* like an additive-free case in long duration more.

[0014] When forming a silver coat on a substrate using the drug solution for silver coat formation of this invention, as a suitable means, it is desirable to take the following means. That is, after defecating a substrate first, the hydrochloric-acid acid-salt-ized first tin solution is passed through contact and the process which carries out conditioning on a substrate.

[0015] 1/10 of some silver solutions which contain a silver nitrate first on the occasion of silver coat formation, i.e., the amount of the silver nitrate applied when carrying out silvering, of amounts thru/or 1/100 The silver solution containing an amount is used and it is silver-nitrate concentration 0.01 mol/L After considering as the thinner solution of order, this is independently contacted on a substrate.

[0016] Subsequently, formation of a silver coat is completed by contacting and making the silver solution containing a silver nitrate which carried out point \*\*, and the reducing solution containing a reducing agent and a strong-base component react simultaneously on a substrate.

[0017] In the method which can form a more uniform silver coat, is made to carry out both-way actuation of the spray nozzle especially conventionally, and forms a silver coat by taking the above-mentioned means, although generating of the geometric thickness unevenness accompanying the actuation poses a problem microscopically, the operation effectiveness of improving such nonconformity substantially is done so.

[0018]

[Example A] Although several examples of operation are illustrated below and this invention is explained, this invention is not limited to this.

[0019] [silver coat formation conditions] — while transporting a substrate, i.e., a pure glass plate, on a conveyor on the following conditions and making the spray gun of a couple reciprocate to a cross direction after pretreatment with a stannous chloride solution — a nozzle edge — respectively — a silver solution and a reducing solution — the regurgitation [ a glass plate top ] — it was made to react and the silver coat was formed. Reaction time was made into 60 seconds, and it washed and dried after the time amount progress concerned, and it was made into the test sample:

[0020]

Glass plate flow velocity It is glass plate temperature by 4.0m/. 23\*\*1 \*\* pretreatment It is contact silver coat formation silver solution discharge quantity about stannous chloride liquid. 131cc/m<sup>2</sup> reducing-solution discharge quantity The drug solution configuration is as [ that it is 131 cc / m<sup>2</sup> ] follows.

[0021] [The drug solution-case 1 for silver coat formation]

A) Silver solution water-solution whole 1000mL Silver nitrate 12g (0.07mol) and 28wt% ammonium hydroxide 21mL are included.

B) reducing solution The water-solution whole 1000mL Gluconic-acid Na 0.015mol and caustic alkali of sodium as 8.4g and an additive — potassium iodide (it mixes in the range of zero to 20 mg) — or Gelatin (It mixes in 0-800mg) or casein Na (it mixes in 0-800mg) or — The multicomputer system of the above-mentioned potassium iodide-gelatin, or multicomputer system of \*\* potassium iodide-casein Na It contains.

[0022] [The drug solution-case 2 for silver coat formation]

A) Silver solution water-solution whole 1000mL Silver nitrate 12g, 28wt% ammonium hydroxide 21mL It contains.

B) the multicomputer system of reducing solution (it mixes in 0-800mg), casein Na (it mixes in 0-800mg), or above-mentioned potassium iodide-gelatin or multicomputer system of \*\* potassium iodide-casein Na is included. The water-solution whole 1000mL Glucitol 0.015mol and caustic alkali of sodium as 8.4g and an additive — potassium iodide (it mixes in the range of zero to 20 mg) — or — Gelatin

[0023] [A trial and measuring method] The rate of plating is calculated from the amount of silver plating / silver amount of supply about the sample obtained by the basis of the above-mentioned drug solution presentation and a test condition by carrying out silver coat formation, and it is a silver plating condition by the scanning electron microscope. (in delicacy, it is precision) It observed. These test conditions are shown in a table 1 and a table 2 with a result.

[0024]

[A table 1]

NO	銀被膜形成用薬液			結 果	
	銀溶液 (硝酸銀の量 g/L)	還元性溶液		銀鍍着 効率 (%)	銀の鍍着状態
		アルカリ+還元剤	添加剤 (量mg/L)		
1	硝酸銀(12) +	NaOH +	KI(ヨウ化カリウム) (0)	40	極めて良好
2	水酸化アンモニウム	グルコン酸Na	" (1)	50	} NO.1と同等ない しやや良好
3			" (2)	62	
4			" (4)	65	
5			" (8)	72	} NO.1よりやや劣 る
6			" (16)	70	
1	硝酸銀(12) +	NaOH +	ゼラチン (0)	40	} NO.1と同等ない しやや良好
7	水酸化アンモニウム	グルコン酸Na	" (50)	58	
8			" (100)	58	
9			" (200)	65	
10			" (400)	68	
11			" (800)	65	
1	硝酸銀(12) +	NaOH +	カゼインNa (0)	40	} NO.1と同等ない しやや良好
12	水酸化アンモニウム	グルコン酸Na	" (50)	52	
13			" (100)	55	
14			" (200)	55	
15			" (400)	57	
16			" (800)	60	
1	硝酸銀(12) +	NaOH +	KI (0) + ゼラチン (0)	40	} NO.1と同等ない しやや良好
17	水酸化アンモニウム	グルコン酸Na	" (1) " (50)	64	
18			" (2) " (100)	71	
19			" (3) " (100)	75	
20			" (5) " (100)	75	
21			" (5) " (300)	71	} NO.1よりやや劣 る
22			" (8) " (800)	71	
1	硝酸銀(12) +	NaOH +	KI (0) + カゼインNa (0)	40	} NO.1と同等ない しやや良好
23	水酸化アンモニウム	グルコン酸Na	" (1) " (50)	60	
24			" (2) " (100)	66	
25			" (3) " (200)	76	
26			" (5) " (500)	72	} NO.1よりやや劣 る
27			" (8) " (800)	70	

[0025]

[A table 2]

NO	銀被膜形成用薬液				結 果	
	銀溶液 (硝酸銀の量 g/L)	還元性溶液		銀鍍着 効率 (%)	銀の鍍着状態	
		アルカリ+還元剤	添加剤 (量mg/L)			
51	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルシトール	KI (0)	60	良好 (NO.1より劣る) } NO.51 と略同等	
52			" (1)	73		
53			" (4)	78		
54			" (16)	72		
51	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルシトール	ゼラチン (0)	60	} NO.51 と略同等	
55			" (50)	65		
56			" (300)	70		
57			" (500)	63		
51	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルシトール	カゼインNa (0)	60	} NO.51 と略同等	
58			" (50)	65		
59			" (200)	70		
60			" (500)	63		
51	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルシトール	KI (0) + カゼインNa (0)	60	} NO.51 と略同等	
61			" (1) " (50)	72		
62			" (2) " (100)	72		
63			" (3) " (200)	70		
64			" (5) " (400)	68		
65			" (5) " (500)	64		
51	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルシトール	KI (0) + ゼラチン (0)	60	} NO.51 と略同等	
66			" (1) " (50)	72		
67			" (2) " (100)	73		
68			" (3) " (200)	71		
69			" (5) " (400)	68		
70			" (5) " (500)	64		

[0026] In addition, the thing and NO.2-NO.27 in which NO.1 does not mix an additive in a table 1 An additive is mixed. Moreover, it sets to a table 2 and is NO.51. The thing and NO.52-NO.70 which do not mix an additive An additive is mixed.

[0027] a table 1 and a table 2 — setting — silver-nitrate 12 g/L = 0.07 mol/L it is — it means that per silver-nitrate 0.1mol is received and the additive had carried out the amount (mg) activity numeric-value x 1.42 times in a table since the silver solution containing a silver nitrate and the reducing solution containing an additive were applied equivalent [ every ]

[0028] [Test result] A test result is as being shown in a table 1 and a table 2, and by gluconic-acid Na as a reducing agent, and the glucitol, although the rates of base plating differ Plating effectiveness improves by addition of potassium iodide, gelatin, Casein Na, or those complexing agents. In the reducing solution which uses especially gluconic-acid Na as a reducing agent, it is potassium iodide. 3 - 5 mg/L (as opposed to silver-nitrate 0.1mol) it becomes the rate of 4.2-7.1mg of potassium iodide — and gelatin 100 mg/L order (as opposed to silver-nitrate 0.1mol) Gelatin 140mg It becomes the rate of order. By making it \*\*\*\*, the best silvering effectiveness is shown and a silver granule child also shows a fine very good plating condition.

[0029]

[Example B]

[Silver coat formation conditions] A substrate, i.e., a pure glass plate, is transported on a conveyor like Example A. Adopt the hydrochloric-acid acid-salt-ized first tin as a pretreatment agent, and processing by the drug solution for silver coat formation is faced this after the regurgitation on a glass plate. The residual silver solution and the reducing solution

were breathed out on the glass plate, respectively, making the spray gun of a couple what diluted the 1/10 section of the below-mentioned silver solution 10 times, making a spray gun reciprocate to a cross direction as a first stage story reciprocate to a cross direction as discharge and a second stage story on a glass plate.

[0030]

Glass plate flow velocity A part for 4.0m/ Glass plate temperature 23\*\*1 \*\* pretreatment Hydrochloric-acid acidity stannous chloride liquid is contacted. Silver coat formation It is formation [0031] by the two following steps. [The drug solution for silver coat formation] The first step silver solution; water-solution whole 1000mL Silver nitrate 1.2g (0.007mol) and 28wt% ammonium hydroxide 2.1mL It contains. It is silver solution discharge quantity per two 1m. 96 cc [0032] Second stage story A silver solution water-solution whole 1000mL Silver nitrate 12g (0.07mol) and 28wt% ammonium hydroxide 21mL are included. It is silver solution discharge quantity per two 1m. 131 cc.

B) Reducing solution water-solution whole 1000mL Gluconic-acid Na 0.015mol, caustic alkali of sodium It is [ 8.4g and ] potassium iodide as an additive. 5mg, casein Na 100mg content. It is reducing solution discharge quantity per two 1m. 131 cc.

[0033] [Example of reference] As an example of reference, a silver solution was not divided, therefore the regurgitation of only the silver solution in a first stage story was omitted, and the rest was processed like Example B and carried out silver coat formation.

[0034] [Test method] It investigated [ example / of reference / Example B and ] about the rate of silver plating, and the plating situation like Example A.

[0035] [Result] The rate of silver plating of Example B is almost same with the example of reference, and 75% of rate of plating was obtained. In addition, according to transmitted light observation, the silver film thickness unevenness considered to be based on reciprocation actuation of a spray gun in the example of reference and punctate silver film thickness unevenness were accepted clearly, but in this example B, these silver film thickness unevenness improves substantially, and the part and the minute light reflex engine performance will be obtained.

[0036]

[Effect of the Invention] According to this invention, it has a high rate of silver plating, a detail and a precise and uniform silver coat are formed, and the effectiveness that a precise reflected image is therefore acquired is done so.

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(54) 【発明の名称】 銀被膜形成用薬液および銀被膜形成方法

(57) 【要約】

【課題】 従来技術に比べ、銀鍍着率が高く、効率的に銀被膜を形成すること、また微細、緻密かつ均一な銀被膜を形成すること。

【解決手段】 アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液にハロゲン化アルカリ類の一種以上、または水溶性蛋白質の一種以上、あるいはそれらハロゲン化アルカリ、水溶性蛋白質を複合して含有せしめた銀被膜形成用薬液、およびそれを用いた銀被膜の形成法。

## 【特許請求の範囲】

【請求項1】アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液にハロゲン化アルカリ類の一種以上を含有せしめたことを特徴とする銀被膜形成用薬液。

【請求項2】硝酸銀の量が0.1molに対し、ハロゲン化アルカリ類の一種以上の量が1~30mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたことを特徴とする請求項1記載の銀被膜形成用薬液。

【請求項3】アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液に水溶性蛋白質の一種以上を含有せしめたことを特徴とする銀被膜形成用薬液。

【請求項4】硝酸銀の量が0.1molに対し、水溶性蛋白質の一種以上が70~1200mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたことを特徴とする請求項3記載の銀被膜形成用薬液。

【請求項5】アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液にハロゲン化アルカリ類の一種以上と、水溶性蛋白質の一種以上とを併存せしめたことを特徴とする銀被膜形成用薬液。

【請求項6】硝酸銀の量が0.1molに対し、ハロゲン化アルカリ類の一種以上の量が1~30mg、および水溶性蛋白質の一種以上が70~1200mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたことを特徴とする請求項5記載の銀被膜形成用薬液。

【請求項7】連続的に移送される清浄な基板上に塩酸性性塩化第一錫溶液を接触、予備処理する工程、銀被膜の形成に際して硝酸銀を含む銀溶液の一部を基板上に先行して接触させる工程、次いで硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とを基板上に同時に接触、反応せしめる工程とからなることを特徴とする銀被膜形成法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明はガラス等の基板上に微細な銀粒子を析出させて銀被膜を形成し、さらに銅被膜、および耐食樹脂被膜を被覆して鏡を製造するにあたり、前記銀被膜を緻密かつ均一に、鍍着効率よく形成する方法に関する。

## 【0002】

【従来技術】アンモニア性硝酸銀を含む銀溶液と、グルコン酸ナトリウム、グルシトール、ブドウ糖、酒石酸、ホルムアルデヒド等の還元剤、および水酸化ナトリウム、水酸化カリウム等の強アルカリ成分を含む還元性溶液とからなる銀被膜形成用薬液を基板上で接触、反応させ、基板上に銀を析出、被膜形成することは知られている。

## 【0003】

【発明が解決しようとする課題】しかし単にこれら成分を接触、反応させるのみでは銀鍍着率が低く、効率的な銀被膜ができず、また微細、緻密かつ均一な銀被膜を形成することはできない。

【0004】本発明は高い銀鍍着率をもって、微細、緻密かつ均一な銀被膜を形成し、よって精密な反射像が得られる銀被膜形成用薬液およびそれをを用いた銀被膜形成法を提供することを目的とする。

## 【0005】

【課題を解決するための手段】本発明は、

1) アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液にハロゲン化アルカリ類の一種以上を含有せしめた銀被膜形成用薬液。

2) 前記において硝酸銀の量が0.1molに対し、ハロゲン化アルカリ類の一種以上の量が1~30mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたこと。

3) アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液に水溶性蛋白質の一種以上を含有せしめた銀被膜形成用薬液。

4) 前記において硝酸銀の量が0.1molに対し、水溶性蛋白質の一種以上が70~1200mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたこと。

5) アンモニア性硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とからなり、これらを反応させ、基板上に銀被膜を形成するための銀被膜形成用薬液において、前記還元性溶液にハロゲン化アルカリ類の一種以上と、水溶性蛋白質の一種以上とを併存せしめた銀被膜形成用薬液。

6) 前記において硝酸銀の量が0.1molに対し、ハロゲン化アルカリ類の一種以上の量が1~30mg、および水溶性蛋白質の一種以上が70~1200mgの量比範囲となるべく、銀溶液および還元性溶液夫々を調製し、両液を基板上で接触させるようにしたこと。

7) 連続的に移送される清浄な基板上に塩酸性性塩化第一錫溶液を接触、予備処理する工程、銀被膜の形成に際して硝酸銀を含む銀溶液の一部を基板上に先行して接触

させる工程、次いで硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とを基板上に同時に接触、反応せしめる工程とからなる銀被膜形成法、から構成される。

#### 【0006】

【発明の実施の形態】銀被膜形成用薬液における銀溶液とは、硝酸銀と水酸化アンモニウムを含む水溶液をいい、銀被膜形成における一方の液として常用される。

【0007】還元性溶液とはグルコン酸ナトリウム、グルシトール、ブドウ糖、酒石酸、ホルムアルデヒド等の還元剤、および水酸化ナトリウム、水酸化カリウム等の強アルカリ成分を含む水溶液をいい、銀被膜形成における他方の液として常用される。

【0008】銀溶液と還元性溶液は、移送される基板、例えば透明ガラス基板上に同時に噴射、混合され、還元反応により銀が析出し、基板上に銀被膜が形成される。なお鏡製造においては同様な化学メッキ法によりさらに銅被膜を形成し、その上に樹脂被覆を施すことにより鏡が完成するものである。

【0009】しかし従来技術においてはメッキ反応の途中で、溶液中に銀コロイドの凝集塊(銀泥と称する)が生ずるため、先述のごとく銀鍍着率が低く、微細かつ緻密な銀被膜を効率的に形成することはできない。本発明においては、前記銀被膜の形成に際し、銀をきめ細かく均一にかつ効率的に膜形成するうえで有効な銀被膜形成用薬液、および銀被膜形成法を提供するものである。

【0010】本発明において、還元性溶液に含有せしめるハロゲン化アルカリ類とはKI、NaI、KBr、NaBr、KCl、NaCl等を、また水溶性蛋白質とはカゼイン、ゼラチンに代表される水に可溶性蛋白質をいう。ハロゲン化アルカリ類は適宜量の混入により、水溶性蛋白質と同様に水溶液中にあって不安定な疎水性の銀コロイドを被覆し、銀泥を防ぐ保護コロイドの役目を果たし、基板への銀の均一な鍍着を促すものである。なお、過量のハロゲン化アルカリを混入すると、再び銀泥が発生して鍍銀効率や鏡の品質低下を招くという弊害が生ずるので注意を要する。

【0011】銀溶液における硝酸銀の濃度は0.1mol/L程度を標準として0.01mol/Lないし1mol/Lの範囲で適宜選択すればよい。還元性溶液におけるハロゲン化アルカリ類や水溶性蛋白質は前記硝酸銀の量、銀溶液と還元性溶液の量比等を勘案して導入するもので、硝酸銀の量0.1molに対し、ハロゲン化アルカリ類が1~30mg、または水溶性蛋白質が70~1200mgの量比範囲となるように調整する。前記範囲において鍍銀効率等において良好な結果が得られる。なお、ハロゲン化アルカリ類と水溶性蛋白質を併存させる場合も上記範囲内とする。

【0012】通常銀溶液と還元性溶液とは、ほぼ等量ずつ採用し基板上で接触、反応させるものであるが、これに限定するものではなく、例えば銀溶液：還元性溶液が

1:1/2 ないし 1/2:1であってもよい。

【0013】銀溶液と還元性溶液との反応時間は、還元性溶液にハロゲン化アルカリ類や水溶性蛋白質等の添加剤を含む場合と、それら添加剤のない場合とで傾向が異なり、無添加の場合は初期の20秒前後までにおいて急速に反応、膜形成し、以降の反応は殆ど進まず、より長時間反応させようとする粗い銀粒子の沈積により膜表面は粗の状態を呈する。添加剤を含む場合は、添加剤の種類、量にもよるが概して初期の40秒またはその前後まで反応が進んで膜形成し、それ以降も緩やかながら反応が進行する。なお、より長時間においては無添加の場合と同様膜表面が粗の状態を呈する傾向にある。

【0014】本発明の銀被膜形成用薬液を用いて基板上に銀被膜を形成するうえで好適な手段としては、次の手段を採ることが望ましい。すなわちまず基板を清浄化したうえで、基板上に塩酸酸性塩化第一錫溶液を接触、予備処理する工程を経る。

【0015】銀被膜形成に際しては、まず硝酸銀を含む銀溶液の一部、すなわち鍍銀するうえで適用する硝酸銀の量の1/10の量ないし1/100の量を含む銀溶液を用い、硝酸銀濃度を0.01mol/L前後のより希薄な溶液としたうえでこれを単独で基板上に接触させる。

【0016】次いで先述したような硝酸銀を含む銀溶液と、還元剤および強アルカリ成分を含む還元性溶液とを基板上に同時に接触、反応せしめることにより銀被膜の形成を完成させるものである。

【0017】上記手段を採ることにより、より均一な銀被膜を形成することができ、特に従来スプレィノズルを往復動作させて銀被膜を形成する方式においては、微視的にはその動作に伴う幾何学的な膜厚むらの発生が問題となるが、そのような不具合を大幅に改善するという作用効果を奏する。

#### 【0018】

【実施例A】以下実施の数例を例示し本発明を説明するが、本発明はこれに限定するものではない。

【0019】〔銀被膜形成条件〕下記条件でコンベア上で基板、すなわち清浄なガラス板を移送し、塩化第一錫溶液で前処理後、一對のスプレーガンを巾方向に往復動させつつノズル端より夫々銀溶液、還元性溶液をガラス板上に吐出、反応させ銀被膜を形成した。反応時間は60秒とし、当該時間経過後洗浄、乾燥して試験試料とした。

#### 【0020】

ガラス板移送速度	4.0m/分
ガラス板温度	23±1℃
前処理	塩化第一錫液を接触
銀被膜形成	

銀溶液吐出量 131cc /m<sup>2</sup>

還元性溶液吐出量 131cc /m<sup>2</sup>

なお、薬液構成は以下のとおりである。

## 【0021】〔銀被膜形成用薬液—ケース1〕

水溶液全体 1000mL に、硝酸銀 12g (0.07mol)、28wt%  
水酸化アンモニウム21mLを含む。

## A) 銀溶液

## B) 還元性溶液

水溶液全体 1000mL に、グルコン酸Na 0.015mol、苛性ソーダ 8.4g、および  
添加剤としてヨウ化カリウム(0～20mgの範囲で混入)、または  
ゼラチン (0～800mgの範囲で混入)、または  
カゼインNa (0～800mgの範囲で混入)、または  
上記ヨウ化カリウム—ゼラチンの複合系、または  
〃 ヨウ化カリウム—カゼインNaの複合系を含む。

## 【0022】〔銀被膜形成用薬液—ケース2〕

水溶液全体 1000mL に、硝酸銀 12g、28wt%水酸化アン  
モニウム 21mLを含む。

## A) 銀溶液

## B) 還元性溶液

水溶液全体 1000mL に、グルシトール 0.015mol、苛性ソーダ 8.4g、および  
添加剤としてヨウ化カリウム(0～20mgの範囲で混入)、または  
ゼラチン (0～800mgの範囲で混入)、または  
カゼインNa (0～800mgの範囲で混入)、または  
上記ヨウ化カリウム—ゼラチンの複合系、または  
〃 ヨウ化カリウム—カゼインNaの複合系を含む。

【0023】〔試験、測定方法〕上記薬液組成、試験条  
件のもとに銀被膜形成し、得られた試料について、銀鍍  
着量／銀供給量から鍍着率を算定し、また走査電子顕微  
鏡により銀の鍍着状態(きめの細かさ、緻密さ)を観察

した。これら試験条件を、結果とともに表1、表2に示  
す。

## 【0024】

## 【表1】

NO	銀被膜形成用薬液				結 果	
	銀溶液 (硝酸銀の量 g/L)	還元性溶液			銀鍍着 効率 (%)	銀の鍍着状態
		アルカリ+還元剤	添加剤	(量mg/L)		
1	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルコン酸Na	KI (ヨウ化カリウム) (0)	40	極めて良好 } NO.1と同等ない しやや良好 } NO.1よりやや劣 る	
2			" (1)	50		
3			" (2)	62		
4			" (4)	65		
5			" (8)	72		
6			" (16)	70		
1	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルコン酸Na	ゼラチン (0)	40	NO.1と同等ない しやや良好	
7			" (50)	58		
8			" (100)	58		
9			" (200)	65		
10			" (400)	68		
11			" (800)	65		
1	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルコン酸Na	カゼインNa (0)	40	NO.1と同等ない しやや良好	
12			" (50)	52		
13			" (100)	55		
14			" (200)	55		
15			" (400)	57		
16			" (800)	60		
1	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルコン酸Na	KI (0) + ゼラチン (0)	40	NO.1と同等ない しやや良好 } NO.1よりやや劣 る	
17			" (1) " (50)	64		
18			" (2) " (100)	71		
19			" (3) " (100)	75		
20			" (5) " (100)	75		
21			" (5) " (300)	71		
22			" (8) " (800)	71		
1	硝酸銀(12) + 水酸化アンモニウム	NaOH + グルコン酸Na	KI (0) + カゼインNa (0)	40	NO.1と同等ない しやや良好 } NO.1よりやや劣 る	
23			" (1) " (50)	60		
24			" (2) " (100)	66		
25			" (3) " (200)	76		
26			" (5) " (500)	72		
27			" (8) " (800)	70		

【0025】

【表2】

NO	銀被膜形成用薬液				結 果	
	銀溶液 (硝酸銀の量 g/L)	還元性溶液			銀鍍着 効率 (%)	銀の鍍着状態
		アルカリ+還元剤	添加剤	(量mg/L)		
51	硝酸銀(12)+ 水酸化アンモニウム	NaOH+ グルシトル	KI	(0)	60	良好(NO.1よりやや劣る) NO.51 と略同等
52			"	(1)	73	
53			"	(4)	78	
54			"	(16)	72	
51	硝酸銀(12)+ 水酸化アンモニウム	NaOH+ グルシトル	ゼラチン	(0)	60	NO.51 と略同等
55			"	(50)	65	
56			"	(300)	70	
57			"	(500)	63	
51	硝酸銀(12)+ 水酸化アンモニウム	NaOH+ グルシトル	カゼインNa	(0)	60	NO.51 と略同等
58			"	(50)	65	
59			"	(200)	70	
60			"	(500)	63	
51	硝酸銀(12)+ 水酸化アンモニウム	NaOH+ グルシトル	KI (0) + カゼインNa (0)		60	NO.51 と略同等
61			" (1)	" (50)	72	
62			" (2)	" (100)	72	
63			" (3)	" (200)	70	
64			" (5)	" (400)	68	
65			" (5)	" (500)	64	
51	硝酸銀(12)+ 水酸化アンモニウム	NaOH+ グルシトル	KI (0) + ゼラチン (0)		60	NO.51 と略同等
66			" (1)	" (50)	72	
67			" (2)	" (100)	73	
68			" (3)	" (200)	71	
69			" (5)	" (400)	68	
70			" (5)	" (500)	64	

【0026】なお、表1においてNO.1が添加剤を混入しないもの、NO.2～NO.27が添加剤を混入したものである。また表2においてNO.51が添加剤を混入しないもの、NO.52～NO.70が添加剤を混入したものである。

【0027】表1、表2において、硝酸銀12g/L=0.07mol/Lであり、硝酸銀を含む銀溶液と添加剤を含む還元性溶液は等量ずつ適用したものであるから、硝酸銀0.1mol当たりに対しては添加剤は表中数値×1.42倍量(mg)を使用したことになる。

【0028】〔試験結果〕試験結果は表1、表2に示すとおりであり、還元剤としてのグルコン酸Na、グルシトルにより、ベース鍍着率は異なるが、ヨウ化カリウム、ゼラチン、カゼインNaまたはそれらの複合剤の添加により鍍着効率は向上し、特にグルコン酸Naを還元剤とする還元性溶液中に、ヨウ化カリウム3～5mg/L(硝酸銀0.1molに対し、ヨウ化カリウム4.2～7.1mgの割合と

なる)、およびゼラチン100mg/L前後(硝酸銀0.1molに対し、ゼラチン140mg前後の割合となる)を併存させることにより最良の鍍銀効率を示し、銀粒子も細かく極めて良好な鍍着状態を示す。

【0029】

〔実施例B〕

〔銀被膜形成条件〕実施例Aと同様にコンベア上で基板、すなわち清浄なガラス板を移送し、前処理剤として塩酸酸性塩化第一錫を採用してこれをガラス板上に吐出後、銀被膜形成用薬液による処理に際しては、第一段階としてスプレーガンを巾方向に往復動させつつ後述銀溶液の1/10部を10倍に希釈したものをガラス板上に吐出し、第二段階として一対のスプレーガンを巾方向に往復動させつつ夫々残余の銀溶液、還元性溶液をガラス板上に吐出した。

【0030】

4.0m/分

23±1℃

塩酸酸性塩化第一錫液を接触

下記の二段階により形成

第一段階

【0031】〔銀被膜形成用薬液〕

ガラス板移送速度

ガラス板温度

前処理

銀被膜形成

銀溶液；水溶液全体 1000mL に、硝酸銀 1.2g(0.007mol)、28wt%水酸化アンモニウム2.1mL を含む。1 m<sup>2</sup> 当たり銀溶液吐出量 96cc

【0032】第二段階

A) 銀溶液

水溶液全体 1000mL に、硝酸銀 12g(0.07mol)、28wt%水酸化アンモニウム21mLを含む。1 m<sup>2</sup> 当たり銀溶液吐出量 131cc。

B) 還元性溶液

水溶液全体 1000mL に、グルコン酸Na 0.015mol、苛性ソーダ 8.4g、および添加剤としてヨウ化カリウム 5mg、カゼインNa 100mg含有。1 m<sup>2</sup> 当たり還元性溶液吐出量 131cc。

【0033】〔参考例〕参考例として、銀溶液を分割せず、従って第一段階における銀溶液のみの吐出を省略

し、あとは実施例Bと同様に処理して銀被膜形成した。

【0034】〔試験方法〕実施例Aと同様に実施例B、参考例について銀鍍着率、鍍着状況について調査した。

【0035】〔結果〕実施例Bの銀鍍着率は参考例と殆ど差異はなく、75%の鍍着率が得られた。なお透過光観察によると、参考例においてはスプレーガンの往復動操作によると思われる銀膜厚むらと、斑点状の銀膜厚むらが明瞭に認められたが、本実施例Bにおいてはこれらの銀膜厚むらは大幅に改善されており、その分、精緻な光反射性能が得られることになる。

【0036】

【発明の効果】本発明によれば高い銀鍍着率をもって、微細、緻密かつ均一な銀被膜を形成し、よって精密な反射像が得られるという効果を奏する。



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